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Tailored Granular Activated Carbon Treatment of Perchlorate in Drinking Water

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ACRONYMS AND ABBREVIATIONS

AA	atomic absorption
AFB	Air Force Base
AFIT	Air Force Institute of Technology
ANSI	American National Standards Institute
bgs	below ground surface
BV	bed volume
CPC	cetylpyridinium chloride
CTAC	cetyltrimethylammonium chloride
CUR	carbon utilization rates
DoD	Department of Defense
DOT	Department of Transportation
DPH	Department of Public Health
DTSC	Department of Toxic Substances Control
EBCT	empty bed contact time
ESTCP	Environmental Security Technology Certification Program
FWC	Fontana Water Company
GAC	granular activated carbon
GPM	gallons per minute
IC-MS/MS	Ion Chromatography Tandem Mass Spectrometry
IRIS	Integrated Risk Information System
ITRC	Interstate Technology and Regulatory Council
IX	ion exchange
kPa	kilopascals
LC/MS/MS	liquid chromatography tandem mass spectrometry
MCL	maximum contaminant level
MGD	million gallons per day
$MgSO_4 \cdot 7\,H_2O$	magnesium sulfate heptahydrate
$NaNO_3$	sodium nitrate
NaOCl	sodium hypochlorite
NAVFAC-ESC	Naval Facilities Engineering Command-Engineering Service Center
NDMA	n-nitrosodimethylamine
NL	notification level
NPDES	National Pollution Discharge Elimination System
NRC	National Research Council

NSF	National Sanitary Foundation
NWIRP	Naval Weapons Industrial Reserve Plant
O&M	operation and maintenance
OMB	Office of Management and Budget
polyDADMAC	poly(dimethyldiallylammonium chloride)
psi	pounds per square inch
PSU	Pennsylvania State University
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
RfD	reference dose
RSSCT	rapid small-scale column test
RWQCB	Regional Water Quality Control Board
SDS	simulated distribution system
Siemens	Siemens Water Technologies
TCE	trichloroethene
TDS	total dissolved solids
TGAC	tailored granular activated carbon
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Perchlorate is a concern in drinking water because of its high solubility and mobility, its effects on thyroid hormone production, and treatment cost. Although perchlorate removal technologies suitable for wellhead application exist, there is a need to develop additional, economical perchlorate removal technologies. In addition, conventional wellhead technologies are specific for perchlorate only and are unable to effectively treat volatile organic compounds (VOCs) that are often co-contaminants. This project demonstrated the application of granular activated carbon (GAC) tailored (TGAC) for the removal of perchlorate in drinking water. The tailoring process adsorbs surfactants with quaternary ammonium groups to GAC, which dramatically increases the perchlorate removal capacity of the GAC, while still allowing the GAC to remove VOCs.

The demonstration site was an operating drinking water treatment plant in Fontana, CA, a city located in the Inland Empire region of southern California. The Inland Empire's perchlorate plume is at least 6 miles long and impacts water supplies in four towns. Two field test installations were implemented; the first consisted of three vessels in series treating 38 gallons per minute (GPM) (0.14 m^3/minute), and the second consisted of six smaller-scale treatment trains treating 1.5 GPM (0.0057 m^3/minute).

1.2 OBJECTIVES OF THE DEMONSTRATION

The primary objectives of the project were to demonstrate: (1) a reliable, cost-effective treatment technology for removing perchlorate from drinking water, (2) removal of both perchlorate and trichloroethene (TCE) simultaneously, and (3) simple system operation and maintenance (O&M) with minimal monitoring. The TGAC system was effective in removing perchlorate to below current regulatory standards for approximately 15,000 bed volumes (BVs) per bed (4- to 5-month bed life). TGAC successfully achieved the perchlorate concentration reduction objective for a total treated volume of approximately 30,500 BVs with two beds in series. Data from two different scales of testing suggest that increases in nitrate and perchlorate influent concentrations reduce, as expected, breakthrough time. Increases in the concentrations of other anions appear, at worst, to only moderately decrease performance.

As a result of recent technological and process improvements, the general cost of conventional ion exchange (IX) systems used to treat perchlorate has declined steadily between 2000 and 2010. This makes it difficult for a new, innovative technology to displace this widely used, accepted alternative. The cost analysis conducted in this project suggests that TGAC is not currently able to economically displace conventional, perchlorate-selective IX resins. There are, however, several options that may improve TGAC cost-effectiveness. The field-scale testing used TGAC prepared from anthracite-based carbon. Although bituminous-based carbon would have been more effective, that change alone would not have been enough to economically displace perchlorate selective resins.

Simultaneous removal of perchlorate and TCE was observed. Breakthrough and saturation both occurred sooner in the TCE spiked system than in the control system. For example, breakthrough occurred 8 to 22% sooner in the TCE spiked system.

Field-scale TGAC operations did not reveal any operational problems directly attributable to the technology. Operations and maintenance activities are likely to be very similar to those required for a similarly sized IX system. However, since IX systems using currently available resins are likely to have a longer time to achieve breakthrough, a greater frequency of monitoring will likely be required for TGAC systems.

1.3 DEMONSTRATION RESULTS

The 38 GPM field-scale TGAC demonstration system operated nearly continuously for 318 days and treated over 16.2 million gallons of perchlorate-impacted groundwater. Six parallel pilot-scale test beds were operated for approximately 6 months each, challenging the technology with varied influent conditions. These challenges included various added ions, pre-disinfection, and TCE as a co-contaminant. Field data were supplemented with 17 rapid small-scale column tests (RSSCTs) performed in the PSU laboratory with Fontana groundwater. TGAC testing with Fontana groundwater showed a shorter bed life to initial perchlorate breakthrough than proportional-diffusivity-based RSSCTs predicted. Laboratory studies indicated that when using RSSCTs to predict perchlorate removal, the best fit to field-scale data relative to initial breakthrough can be obtained using a mathematical approach intermediate between proportional and constant diffusivity.

For these trials, an anthracite-based GAC was preloaded with cetylpyridinium chloride (CPC). Studies conducted after the completion of the Fontana field-scale work show that the anthracite-based GAC is inferior in performance to bituminous-based GAC because of differences in porosity structure. The CPC tailoring agent was selected for this field test based on previous data and for ease of permitting. However, other tailoring agents such as Arquad 2C-75 may provide better perchlorate selectivity over competing anions like nitrate. Based on results available to date, TGAC technology may be best suited for use on aerobic waters with low nitrate concentrations and with VOCs as co-contaminants. Additional research to optimize tailoring agents to particular groundwater chemistries may be warranted.

1.4 IMPLEMENTATION ISSUES

Regulatory requirements for TGAC technology may include a discharge permit (and possibly treatment) for disposal of backwash water and other process water, and permitting as required in the state of operation prior to use as a drinking water technology. Department of Transportation (DOT) and Resource Conservation and Recovery Act (RCRA) regulations apply to disposal of spent TGAC and potentially to spent particulate filters if VOCs are treated. From the end user's perspective, perceived or potential limitations not found with other treatment technologies include (1) a lower perchlorate capacity than most IX resins, requiring more frequent change-outs and (2) a lower hydraulic loading rate or a longer contact time than IX, requiring more or larger vessels to treat a given flow rate of water, which increases capital cost and treatment system footprint. If applied to a mixed-contaminant water, e.g., perchlorate and VOCs, the contaminants may reach breakthrough at different times, which would require an early change-out, and thus a reduced capture efficiency for VOCs or perchlorate as compared to two separate media. Finally, TGAC may leach small concentrations of the tailoring agent into treated water, possibly requiring the addition of a "guard" bed to capture residual tailoring agent.

2.0   INTRODUCTION

This report describes an evaluation of a wellhead perchlorate treatment process for drinking water using TGAC. The demonstration site was at an operating municipal water treatment plant owned by FWC, in Fontana, CA. ARCADIS was the prime contractor (contract #W912HQ-06-C-005), with Siemens Water Technologies (Siemens), PSU, and AFIT as partners. Funding and oversight were provided by ESTCP and NAVFAC-ESC. The project was funded under a special congressionally directed program to ESTCP for wellhead perchlorate treatment. This work was contracted through the Corps of Engineers in Alexandria, VA, and overseen by NAVFAC-ESC. This cost and performance report summarizes the project; a full final report providing more details on the technology, test procedures, and data is available.

2.1   BACKGROUND

Perchlorate is a concern in drinking water because of its high solubility and mobility, known effects on thyroid hormone production, and treatment cost. The need for perchlorate treatment is especially acute in Southern California's Inland Empire region. The Inland Empire's perchlorate plume is at least 6 miles long and impacts four towns' water supplies, resulting in impairment of approximately 62,000 acre-ft (7.6×10^7 m^3) per year of potable water.

Although perchlorate treatment technologies suitable for wellhead application exist, there is a need to develop additional, economical perchlorate treatment technologies. In addition, conventional wellhead technologies are specific for perchlorate only and are unable to effectively treat VOCs that are often co-contaminants. This project demonstrated the application of GAC that is tailored (TGAC) for the removal of perchlorate for drinking water applications. The tailoring process adsorbs surfactants with quaternary ammonium groups to GAC, which dramatically increases the perchlorate removal capacity of the GAC, while still allowing the GAC to remove VOCs. Perchlorate and TCE are known co-contaminants at several Department of Defense (DoD) sites, including Vandenberg Air Force Base (AFB), CA; Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, TX; Aerojet Corporation, Rancho Cordova, CA; and in a regional-sized plume in Riverside and San Bernardino, CA, in the Inland Empire area.

The TGAC technology was originally developed by PSU. PSU has teamed with Siemens to further develop the technology and move it toward commercialization. This technology has not yet been permitted for use in drinking water applications but has been tested at field-scale for environmental remediation applications (Graham et al., 2004; Graham, 2006).

The demonstration site was an operating drinking water treatment plant in Fontana, CA, a city located in the Inland Empire region. Two field test installations were implemented; the first consisted of three vessels in series treating 38 GPM (0.14 m^3/minute), and the second consisted of six smaller-scale treatment trains treating 1.5 GPM (0.0057 m^3/minute).

2.2   OBJECTIVES OF THE DEMONSTRATION

The primary objectives of the project were to demonstrate the following: (1) a reliable, cost-effective treatment technology for removing perchlorate from drinking water, (2) removal of

both perchlorate and TCE simultaneously, and (3) simple system operation and maintenance with minimal monitoring.

The TGAC system was effective in removing perchlorate to below current regulatory standards for approximately 15,000 BVs (4- to 5-month bed life at the flow rates used in this demonstration). As a result of recent improvements in the perchlorate capacity and decreases in the market price of perchlorate selective IX resins, the operating cost of conventional single use IX systems used to treat perchlorate has declined steadily between 2000 and 2010. This makes it difficult for an innovative technology to displace this widely-used, regulatorily accepted alternative. The cost analysis conducted in this project suggests that TGAC is not currently able to economically displace conventional IX resins. There are, however, several options that may improve TGAC cost-effectiveness.

Simultaneous removal of perchlorate and TCE was observed. Breakthrough and saturation both occurred sooner with the TCE spiked system than with the control system. For example, breakthrough occurred 8 to 22% sooner in the TCE spiked system.

Field-scale TGAC operations did not reveal any problems directly attributable to the technology. During drinking water treatment with TGAC, the operations and maintenance activities will likely be very similar to those required for a similar-capacity IX system. However, since IX systems using currently available resins will likely have a longer time to achieve breakthrough, a greater frequency of monitoring will likely be required for a TGAC system.

This demonstration was conducted to provide information valuable to water purveyors who draw groundwater from the area of the regional plume underlying the Fontana site. The demonstration was also intended to inform the regulatory community that is overseeing perchlorate wellhead treatment and remediation. In addition, the demonstration design addressed ESTCP's goal of offering accurate cost projections, for a broad range of perchlorate contaminant and competing species concentrations that allow cost evaluations for other groundwater applications worldwide.

2.3   REGULATORY DRIVERS

Throughout the United States, perchlorate standards or advisory levels are still evolving and currently range from 1 to 18 micrograms per liter (µg/L). No enforceable federal standard has yet been established; however, the U.S. Environmental Protection Agency (USEPA) adopted the National Research Council's (NRC) reference dose (RfD) of 0.0007 milligrams per kilogram per day (mg/kg/day) (posted on the Integrated Risk Information System [IRIS] http://www.epa.gov/IRIS/) in February 2005, and USEPA is working to determine if a maximum contaminant level (MCL) should be established. In January 2009 USEPA issued an interim health advisory level for perchlorate in drinking water of 15 µg/L. The California Department of Public Health (DPH) finalized an MCL for perchlorate in drinking water of 6 µg/L on October 18, 2007. California DPH further requires that any treatment technology used in drinking water applications must have National Sanitary Foundation (NSF) 61 certification.

3.0 TECHNOLOGY

3.1 TECHNOLOGY DESCRIPTION

3.1.1 Properties of GAC and Tailoring Process

GAC has a long and successful history of use in drinking water treatment settings because of its high organic removal efficiency. In the United States, GAC is generally used to address taste and odor problems or to remove VOCs from groundwater. The TGAC technology uses GAC as a substrate upon which a surfactant such as CPC can be preloaded, to remove an inorganic ionic species such as perchlorate. The perchlorate capacity of GAC is normally low.

Activated carbon is created by thermally and chemically treating carbon-based solids, such as bituminous coal, anthracite coal, lignite coal, coconut shells, or wood. The carbon layer surfaces are generally uncharged (hydrophobic), and they thus repel water and charged inorganic species such as perchlorate. However, the uncharged carbon surfaces are ideally suited to sorb surfactants. By preloading the activated carbon with N-surfactant that consists of alkyl quaternary amines or other active nitrogen groups, a noncharged surface is converted into a highly plus-charged matrix. This creates a unique rigid material, which offers properties that are well suited for capturing the perchlorate anion.

Several authors have explored the sorption and binding of cationic surfactants onto graphite, cellulose, clay, quartz, titanium dioxide, zeolites, soils, and membranes. However, the project team is not aware of others who have explored preloading activated carbons with N-surfactants to enhance anion removal. To date, PSU and Siemens have used several GAC tailoring agents for the perchlorate sorption during technology development. CPC was chosen as the tailoring agent for this project because of previous performance and the fact that it is an approved ingredient in many commercially available brands of mouthwash. This fact should facilitate obtaining American National Standards Institute (ANSI) and NSF certification of the tailoring agent, which is required by the DPH for full-scale application of a drinking water treatment technology.

Although an anthracite-based GAC was used in this demonstration. Siemens and PSU have tested other GACs for use in the manufacture of TGAC. In proof-of-concept bench-scale trials performed at PSU and during a field-pilot demonstration at Redlands, CA, it has been shown that bituminous GAC can be preloaded with N-surfactants in a manner that dramatically increases its capacity to remove perchlorate. The cationic surfactants used in this project contain a quaternary ammonium or pyridinium functional group (Parette and Cannon, 2005a; Parette, 2005c); the same functional groups have been shown to remove perchlorate in IX technology (Clifford et al., 2004).

3.1.2 Schematic Diagram of the Technology

During the demonstration project two field tests were conducted at 38 GPM beds and six 1.5 to 3 GPM beds designed to challenge the system with various additives to the influent. The 38 GPM system consisted of three vessels operating in series, as identified in Figure 1.
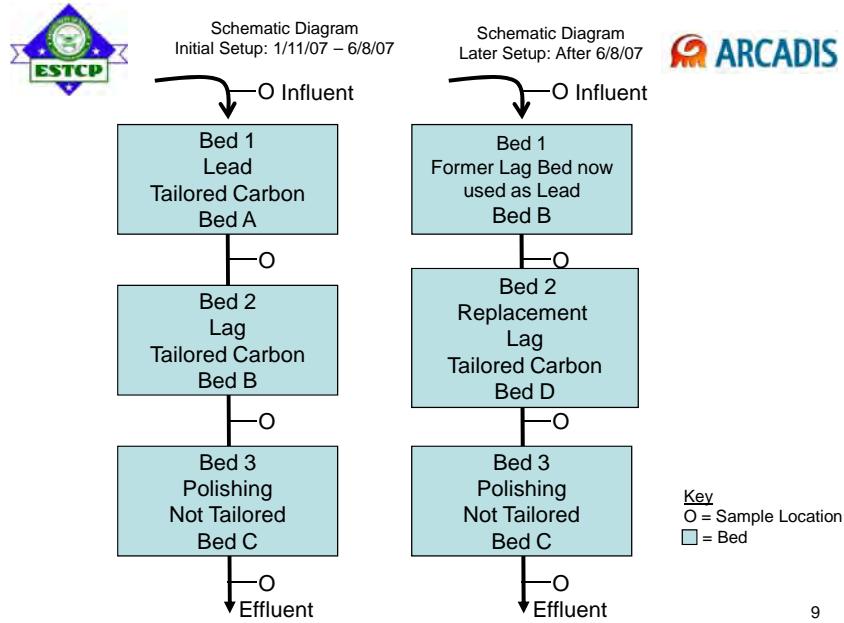
Figure 1. Bed ordering/operational diagram of 38 GPM systems at Fontana, CA.

All three vessels were operated in a down-flow configuration. This system was designed to treat water at a flow rate of approximately 37.5 GPM (0.14 m^3/min), which corresponds to a 10 minute empty bed contact time (EBCT) in each vessel (total EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC).

The other field-scale configuration, consisting of six sets of three vessels operating in series, is shown in Figure 2. The first two vessels in each set were stratified with TGAC overlying conventional GAC in the same chamber. GAC was present to remove residual TCE and/or tailoring agent, if present. The third vessel in each series contained conventional GAC as a precaution. These vessels were designed to operate in a down-flow configuration with a 10-minute TGAC EBCT and a 5-minute GAC EBCT, which corresponds to a flow rate of approximately 1.5 GPM. Thus with two stratified beds in series, the system had a total design EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC, which was designed to be the same as the 38 GPM system. These were implemented to test varying arrays of common competitive species such as nitrate, sulfate, and TCE.
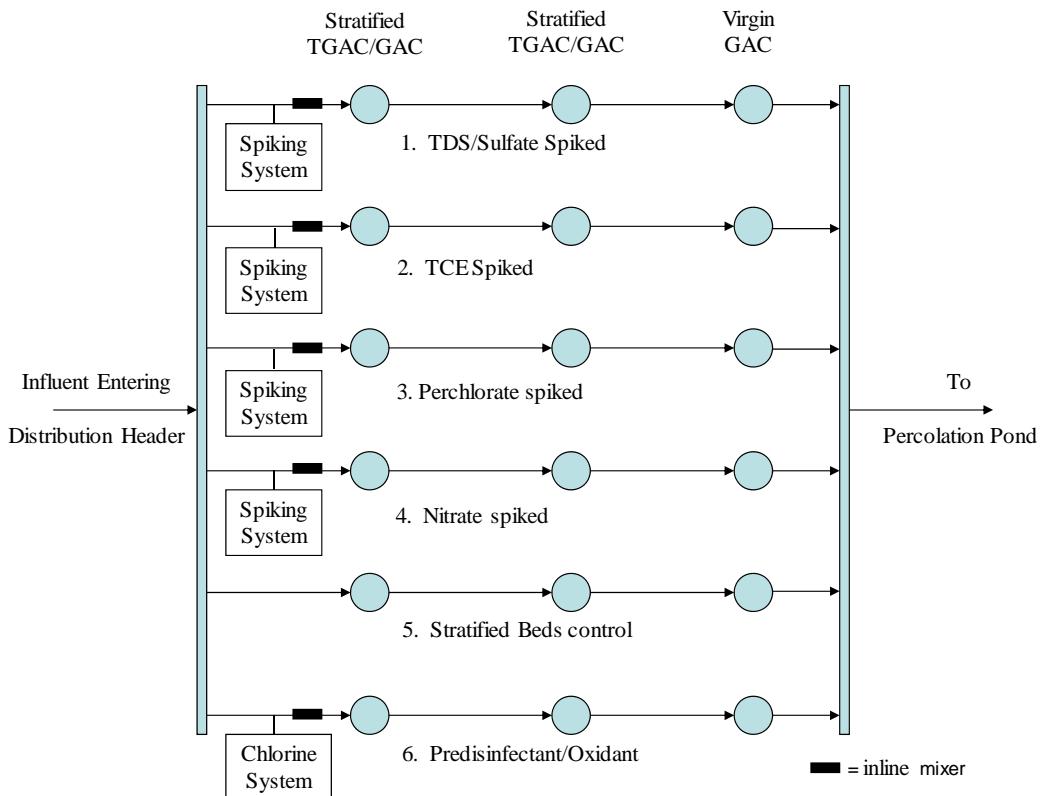
Figure 2. Flow schematic for six small-scale TGAC treatment trains.

3.1.3 Chronological Summary of TGAC Technology Development to Date

Recognizing a need to improve the removal of perchlorate in GAC systems, PSU looked at cationic surfactants as a tailoring agent, starting with a polymer known as poly(dimethyldiallylammonium chloride) (polyDADMAC). It was noted that tailoring with low molecular weight blends of polyDADMAC led to higher perchlorate capacity in GAC than with their high molecular weight counterparts (Parette, 2004). After these initial results PSU worked to improve the tailoring process of the GAC as well as to find smaller molecule cationic surfactants. Thus tailoring with quaternary ammonium monomer species was investigated. A number of quaternary ammonium monomers were used and the adsorption capacity for GAC after they were preloaded with any one of these monomers was as great as 33 times that of virgin carbon. Further studies were reported by Parette (2004) Parette and Canon (2005), and Parette et al. (2005).

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Reviews of currently available technologies for perchlorate in drinking water and for ex situ treatment of groundwater have been published recently (ITRC [Interstate Technology and Regulatory Council], 2005, 2008; USEPA, 2005). Although IX and bioremediation methods have been shown to be effective technologies to treat perchlorate contaminated water, the use of TGAC to treat microgram per liter concentration of perchlorate has some advantages over these methods. Of the current widely used methods, TGAC is most similar to IX, the most common technology in use.

Potential advantages of TGAC over other perchlorate treatment technologies include:

- Ability to simultaneously treat both perchlorate and organic co-contaminants. This could provide cost savings when compared to IX, particularly in mixed perchlorate/VOC applications that are common in the Inland Empire.

- Simple installation and operations and maintenance.

- Can be implemented at existing VOC and perchlorate treatment facilities.

- Potential to reactivate spent TGAC, which would destroy perchlorate and/or VOCs, be retailored, and allow the TGAC to be reused. (Chen and Cannan et al., 2005).

- Does not have secondary water quality concerns associated with IX (e.g., nitrate and/or sulfate sloughing during start up).

- Microbial treatment processes are less favorable for processing low concentrations of perchlorate. Also, some utilities are not amenable to microbial methods for drinking water.

Perceived or potential disadvantages of TGAC include the following:

- Lower perchlorate capacity than most IX resins. This limitation may become more pronounced as new, higher capacity perchlorate-selective IX resins are developed.

- Requirement for a lower hydraulic loading rate or a longer contact time than IX, and thus more or larger vessels for a given flow rate of water.

- Less selectivity over certain competing anions such as nitrate than the most advanced selective IX resins.

- If applied to mixed-contaminant water (e.g., perchlorate and VOCs) the contaminants may reach breakthrough at different times, and thus reduced capture efficiency for VOCs or perchlorate than with two separate media.

- Small concentrations of tailoring agent may be leached into treated water, requiring a polishing GAC bed.

- Perchlorate may be released after the bed has reached perchlorate saturation.

- Potential for nitrate or sulfate rollover.

- Potential issue for any exchange based media, including TGAC, is the impact of some reduced species (i.e., thiosulfate) on performance.

The combined experience at bench-scale and field-scale at the Redlands and Fontana sites indicates that the surfactant-tailored GAC is most suitable for removing perchlorate when the nitrate levels are low. The dual surfactant tailored/conventional GAC combination is likely to be the more economical when removing both perchlorate and VOCs.

4.0   PERFORMANCE OBJECTIVES

The overall goal of this project was to evaluate the technical and economic performance of the TGAC technology for wellhead treatment of groundwater supplies. Specific objectives and how they were met are summarized in Table 1.

Table 1. Performance objectives for TGAC perchlorate treatment train.

Performance Objective	Data Requirements	Success Criteria	Result
Quantitative Performance Criteria			
Meet California perchlorate MCL	Perchlorate concentration in treated effluent	<6 µg/L perchlorate with CPC-tailored TGAC	Yes , for 15,000 BV
Time to saturation of TGAC/GAC unit	Volume at perchlorate saturation (90% of influent concentration)	Allows 6 months of treatment in reasonably sized vessel	No, data showed 4 to 5 months of treatment.
Pressure drop across system	Differential pressure drop across three-bed demonstration system from startup to perchlorate breakthrough	<10 pounds per square inch (psi) (69 kilopascals [kPa])	No, pressure drops were typically higher (average ~20 psi, 138 kPa).
Reduced treatment costs	Cost per pound of TGAC and GAC and per volume treated	Reduce treatment costs significantly over IX technology by reducing use of lower priced TGAC compared to resin	Cost not reduced compared to current IX prices.
Demonstrate TCE removal in laboratory RSSCT studies	TCE concentration in column effluent	<5 µg/L TCE	Plan was changed and TCE removal was demonstrated in field-scale testing and in a laboratory isotherm test.
Determine capacity for removal and competition of other anions – nitrate, sulfate, chloride, bicarbonate, and other reduced sulfur species	Anion concentrations in treated effluent	Document anion removal & competition	Yes
Removal of TCE present as a co-contaminant	TCE concentration in treated effluent	Below TCE MCL of 5 µg/L	Yes
Identify & assess scaling parameters	Operator's assessment, comparison of results from multiple test scales	Identify scale-up issues	Yes
Operator time requirements	Man hours and cost to operate the 38 GPM system per acre-ft of water treated	Document operator time & labor costs	Yes
Reliability	Time required for adjustments and restarts of the 38 GPM system	Minimal down time	Yes, considering only down time attributable to the technology, reliability was 98.2%. Some additional down time was attributable to FWC's well operations.

Table 1. Performance Objectives for TGAC Perchlorate Treatment Train (continued)

Performance Objective	Data Requirements	Success Criteria	Result
Qualitative Performance Criteria			
Reduced treatment costs	Life-cycle cost	Reduce treatment costs significantly over conventional IX technology by reducing adsorbent media costs	No, cost of conventional IX treatment has decreased substantially and TGAC had a lower treatment capacity during field-scale operation than anticipated.
Flow rate and pressure fluctuations	Flow rate and pressure system measurements	Document response to flow and pressure fluctuations	Yes
Ease of operation & maintenance	Field technician feedback	Same as or better for operator than current IX systems	Yes
Waste generation	Generated waste volume, cost	Document how the spent TGAC and other waste streams are disposed	Waste TGAC volume essentially equivalent to volume used. Disposal is not yet complete but intention is to landfill in Beatty, NV.

5.0   SITE DESCRIPTION

5.1   SITE LOCATION HISTORY

The field demonstration was performed at the existing FWC perchlorate treatment facility located in Fontana, CA, adjacent to groundwater production wells FWC-17B and FWC-17C. The FWC full-scale perchlorate treatment system at the same site utilizes one-pass (non-regenerable) IX that is comprised of five parallel trains of lead-lag vessel pairs (a total of 10 IX vessels), and has a maximum treatment capacity of approximately 5000 GPM (0.3 m^3/s). Production wells FWC-17B and FWC-17C pump water through the treatment system and then to the FWC's distribution system reservoir. Currently, the IX system utilizes Purolite A-530E resin. The site also has a National Pollution Discharge Elimination System (NPDES)-permitted percolation pond that is used to discharge water generated during resin change-outs and well blow-down. A site location map is provided as Figure 3.

5.2   SITE GEOLOGY/HYDROGEOLOGY

The demonstration site houses two groundwater production wells, a drinking water reservoir, a percolation pond, and a perchlorate treatment system. Groundwater is extracted from the Chino formation. Based on information from the U.S. Geological Survey, the site is likely to be high in dissolved oxygen (>50% of saturation), with dissolved organic carbon below 1 mg/L, phosphorous below 0.04 mg/L, and with alkalinities between 130-180 mg/L as CaCO$_3$. Production wells are screened from 500 to 860 ft below ground surface (bgs) and from 500 to 920 ft bgs. Wells are managed for production and nitrate concentration using pumping time and inflatable packers.

5.3   CONTAMINANT DISTRIBUTION

The site sits above a large regional perchlorate plume that is unrelated to past or current site operations and is located in a light industrial/residential area of Fontana, CA. Perchlorate concentrations ranged from 8.2 to 24 µg/L for well 17B and 4.0 to 19 µg/L for well 17C from June 1998 to January 2007.

Figure 3. Site location map.

6.0   TEST DESIGN

6.1   CONCEPTUAL EXPERIMENTAL DESIGN

The experimental design associated with this project was intended to transition the TGAC technology from laboratory testing to field implementation. During this project, a series of TGAC experiments were conducted with sufficient performance monitoring to delineate the functional lifetime of the media and generate data for the California regulatory approval process. From an experimental design perspective, the demonstration consisted of three main experimental components─the 38 GPM system, the six condition pilot scale system (1.5 to 3.0 GPM per system) and bench scale tests using RSSCT. The output from these three experimental components was then coupled to a predictive model that will expedite the screening of future sites for the practicality and economics of TGAC implementation.

The demonstration had a 20-month overall duration (12 months of testing at 38 GPM scale partially overlapping with 12 months of testing at 1.5 to 3.0 GPM scale). The project team also designed the project to gather data on the scalability of the system. The scaling of this technology has previously employed the RSSCTs and scaling equations for proportional diffusivity by Crittenden et al. (1991).

A 38 GPM scale field pilot system was a major component of the TGAC demonstration designed to evaluate performance over an extended demonstration interval. An additional component of the experimental design for this demonstration project was the PSU evaluation of water quality parameter effects on TGAC performance through the application of RSSCTs spiked to an array of concentrations of various anions and pH conditions. The results of the RSSCTs and field sensitivity test were inter-compared and used to support mathematical modeling by AFIT. Six additional smaller-scale field column tests (in the Six-Condition Pilot-Scale Field System) were performed to test system response to variations of selected groundwater chemistry parameters.

Compilation and analysis of the data resulting from the 38 GPM system, the RSSCT results, and the small-scale field pilot tests document TGAC performance and reliability over a broad range of contaminant concentrations and realistic groundwater chemistries. Lastly, the results of this demonstration may be compared to the results of previous TGAC demonstrations at Redlands and a Massachusetts site to provide further insight into how the technology's critical design and operating factors vary with differing combination of general influent chemistry.

6.2   BASELINE CHARACTERIZATION

This demonstration project was conducted on groundwater from a perchlorate-impacted aquifer that is contaminated on a regional scale. The chemistry of the groundwater that was used in the demonstration is typical of groundwater that is treated in the California Inland Empire; however, the average perchlorate concentration is slightly lower, and the average nitrate concentration is slightly higher than at other perchlorate treatment systems in the area. For the purposes of this project, the baseline was defined as the untreated water as pumped during routine operation from wells FWC-17B and/or FWC-17C. During the demonstration, the mean perchlorate concentration among 58 measurements was 8.3 µg/L (as compared to the California MCL of 6 µg/L), with a range of 5.1 to 12.6 µg/L. The influent nitrate mean was 34.5 mg/L as nitrate.

6.3   TREATABILITY OR LABORATORY STUDY RESULTS

RSSCTs conducted by the PSU team focused on how other anions compete with perchlorate in a manner that diminishes the capacity of the cationic surfactant-tailored GAC for removing perchlorate. The design of the bench-scale experiments employed the RSSCT scaling equations for proportional diffusivity by Crittenden et al. (1991). If the proportional diffusivity model holds, then a properly designed RSSCT will accurately predict field-scale performance. When employing virgin GAC, PSU has demonstrated that proportional diffusivity is indeed the proper model. However, when employing TGAC, there were some possible distinctions.

There were several problems that prevented running RSSCTs with TCE and perchlorate concurrently during this work. The largest problem was that an RSSCT designed for perchlorate works on proportional diffusivity, while an RSSCT designed for TCE works on constant diffusivity. This means that an RSSCT cannot be compatibly run on both constituents simultaneously. Thus, we chose to evaluate the effects of the concurrent operation using the field-scale 1.5 GPM beds and isotherm information.

The results of 17 RSSCTs show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment of pH 4 was 50% greater than the natural occurring pH of the groundwater at 8, and 75% greater than at a pH of 10. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration (60 mg/L) reduced the removal of perchlorate by 17%; and a nitrate concentration of 100 mg/L reduced removal by 53%. Sulfate, thiosulfate, chloride, and bicarbonate did not affect the adsorption of perchlorate to TGAC sites up to the MCL. The bench-scale experiments also showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7.

The effects of the tailoring agent on TGAC's ability to remove TCE were studied in the form of sorption isotherms. Cetyltrimethylammonium chloride (CTAC), (a tailoring agent) exhibited minimal influence on TCE adsorption, indicating there were no differences in the capacity of TGAC and ordinary GAC to adsorb TCE when there were high concentrations of TCE present.

6.4   FIELD TESTING

6.4.1   38 GPM System Operations

The larger-scale (38 GPM) portion of the field-scale test consisted of one set of three vessels operating in series (Figure 1). Each of the first two vessels of the treatment train contained approximately 50 cu ft (1.4 cu m [m^3]) of TGAC, while the third contained the same volume of conventional GAC, to remove residual tailoring agent, if any, in the treated water. This system treated water at a target design flow rate of approximately 37.5 GPM (0.14 m^3/min), which corresponds to an approximate 10 minute EBCT in each vessel (a total EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC). The system operated nearly continuously for approximately 318 days, treating over 16.2 million gallons of perchlorate-impacted groundwater.

Initial perchlorate breakthrough on Bed A was observed at ~12,400 BVs. This bed continued operating until perchlorate saturation (defined as an effluent perchlorate concentration of 90%, or more, of the influent perchlorate concentration) was observed at ~17,300 BVs. Bed D was placed

in service at 18,000 BVs as the new lag bed while Bed B became the lead bed (Figure 1). A low level of perchlorate breakthrough from Bed D was observed between 21,000 and 26,000 BVs into the demonstration before the concentration reverted to nondetect. Breakthrough clearly occurred at 35,000 BVs and saturation was reached by 40,000 BVs.

Overall the system operated at 97% uptime. Ignoring downtime unrelated to the TGAC system, the uptime efficiency was 98%.

6.4.2   Six Condition Pilot-Scale System Operation

The smaller Six-Condition Pilot-Scale System consisted of six parallel, pilot-scale beds, each with three down-flow vessels operating in series (Figure 2). Both the first and second vessels in each series contained stratified TGAC/GAC beds with 2.1 cu ft of TGAC in the lead layer (on top), and 1.0 cu ft of conventional GAC in the second layer (on bottom) to remove residual TCE (from spiking) and/or tailoring agent, if present. Similar to the field-scale system, a third vessel containing 3.1 cu ft of conventional GAC was utilized as a guard bed. Most sampling was conducted after the first two stratified beds but ahead of the guard bed.

The six trains included a stratified bed control and five spiking systems with holding tanks, mixers and metering pumps, for TCE, increased perchlorate concentration, nitrate, total dissolved solids (TDS)/sulfate, and disinfectant/oxidant. The six pilot-scale vessels were originally designed to operate at the same 10-minute TGAC EBCT as the larger 38 GPM system, which corresponded to a flow rate of approximately 1.5 GPM (0.0057 m^3/minute). However, a preliminary analysis of bench-scale data suggested that a higher flow rate could provide a longer bed life because the beds would be less subject to short circuiting. Very slow flow rates in media systems might incur channeling because of a lack of friction head to distribute flow. Thus, during the test the flow rate was increased to approximately 3.0 GPM in the Stratified Bed Control and Disinfectant/Oxidant Train to decrease the TGAC EBCT to ~5 minutes in each bed. Flow rate control was significantly more difficult in the smaller pilot-scale systems than in the 38 GPM systems.

6.4.2.1   Stratified Beds Control—No Spiking Agent

This treatment train was designed to provide the baseline for comparison with the other field tests and RSSCT results. The control was fed unamended Fontana site water and had no spiking system.

6.4.2.2   TCE Spiked

Perchlorate and TCE are common co-contaminants in the Inland Empire of southern California. This treatment train was spiked with TCE with a target concentration of 50 µg/L. The variability of TCE concentration was extreme during the period of operation of the original spiking system. The spiking system was then revised and the first bed was taken offline so that a test could be conducted with a "fresh" bed that had not been affected by the irregular spiking levels. After revisions were made, the average TCE concentration in the influent water to the beds was 42.5 µg/L.

6.4.2.3 Perchlorate Spiked

The increased perchlorate concentration train increased the perchlorate concentration with a target concentration of 200 µg/L in order to demonstrate the technology's response to a higher concentration of this key contaminant. The spiked perchlorate concentration averaged 315 µg/L for the duration the demonstration. The train operated nearly continuously for approximately 197 days, with an average flow rate of 1.5 GPM.

6.4.2.4 Nitrate Spiked

Nitrate is a competitive anion with perchlorate for sorption sites on TGAC and is known from bench-scale testing to significantly decrease perchlorate capacity. The target concentration was 50 mg/L (as nitrate), the treatment train spiking system delivered sodium nitrate ($NaNO_3$) solution to attain the target nitrate concentration. The nitrate train ran continuously for approximately 212 days at an average flow rate of 1.4 GPM.

6.4.2.5 Pretreatment Disinfectant/Oxidant

A number of drinking water treatment systems disinfect groundwater with an oxidant (typically chlorine based) prior to the application of GAC. The effect(s) of upstream chlorination on perchlorate removal by TGAC is unknown. The influent of this pilot-scale disinfectant/oxidant train was designed to pre-treat with between 0.15 and 0.3 mg/L free chlorine as sodium hypochlorite (NaOCl) to simulate a full-scale drinking water treatment operation. The treatment train incorporated approximately 30 minutes of contact time prior to being pumped through the TGAC bed. It operated nearly continuously for approximately 179 days, with an average flow rate of 2.8 GPM.

6.4.2.6 TDS/Sulfate Train

TDS may compete with perchlorate for TGAC sorption sites and thus impacts perchlorate capacity. This treatment train was spiked with magnesium sulfate heptahydrate ($MgSO_4 \bullet 7\ H_2O$) to approximately 1200 mg/L TDS. This treatment train was spiked with an average TDS concentration of 969 mg/L. The TDS train operated nearly continuously for approximately 218 days, at an average flow rate of 1.3 GPM (13.2 minute EBCT).

6.4.3 Simulated Distribution System (SDS) Testing

SDS testing was conducted on the TGAC system effluent to determine the potential for disinfection byproduct generation following disinfection with bleach. Bench-scale testing was performed on samples of TGAC effluent in treatments dosed with bleach and/or CPC, and controls.

6.4.4 Schedule

A schedule of the major testing phases is provided as Figure 4.

ID	Task Name	Half 2, 2006	Half 1, 2007	Half 2, 2007	Half 1, 2008	Half 2, 2008
1	37 GPM System					
2	**Six Small Field-scale Systems**					
3	Control					
4	TCE					
5	Perchlorate					
6	Nitrate					
7	Hypochlorite					
8	TDS					
9	RSSCT					
10	AFIT Model Development					
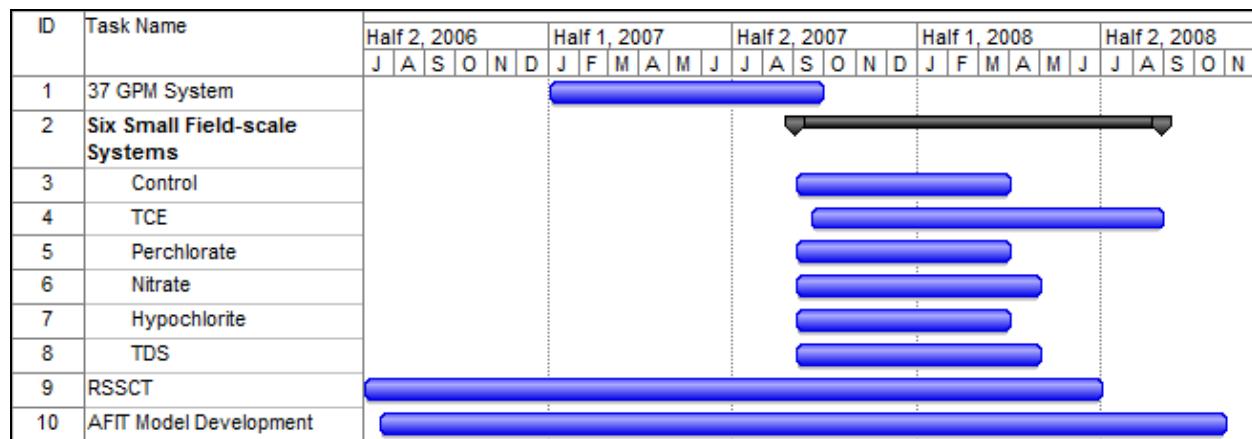
Figure 4. Testing schedule.

6.5 SAMPLING AND ANALYSIS METHODS

Samples were discrete grab samples. Primary sample locations for the 38 GPM system were the influent (taken before the pre-filter), Effluent 1 (after first TGAC bed), Effluent 2 (after second TGAC bed) and Effluent 3 (after third, conventional GAC bed). The primary sample ports used in the six condition pilot-scale system were the common six column influent manifold, individual bed influents, Effluent 1 (after first stratified bed) and Effluent 2 (after second stratified bed).

The primary perchlorate analytical method was USEPA Method 314.0. Because of the potential limitations of this method, 5% of the samples were also subjected to perchlorate analysis by USEPA Method 332.0 (ion chromatography-tandem mass spectrometry [IC-MS/MS]).

Cation analyses were performed using atomic absorption (AA) spectrometry and followed quality assurance/quality control (QA/QC) procedures detailed in Part 3000 of Standard Methods for the Examination of Water and Wastewater, 20th Edition.

CPC was analyzed by liquid chromatography/tandem mass spectrometry (LC/MS/MS) with a seven-point calibration curve. PSU screened samples for CPC and provided additional data for high concentration samples using the titration method of Tsubouchi et al. (1981). Siemens also used this method in the field during system startup.

6.6 SAMPLING RESULTS

6.6.1 Bench-Scale Test Results

Results from the 17 RSSCTs show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment of pH 4 was 50% greater than the natural occurring pH of the groundwater at 8 and 75% greater than at a pH of 10. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration (60 mg/L)

reduced the removal of perchlorate by 17%; and a nitrate concentration of 100 mg/L reduced removal by 53%. Sulfate, thiosulfate, chloride, and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to their MCL. Also the bench-scale experiments showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7.

6.6.2   38 GPM Demonstration-Scale System Sampling Results

6.6.2.1   Perchlorate Results

Figure 5 shows individual bed breakthrough curves. Perchlorate breakthrough was observed at 12,000 BVs for Bed A, used in the lead position. Breakthrough was observed at 20,000 BVs for Bed B, the initial lag bed. Saturation was observed at approximately 16,000 BVs for Bed A (measured through one bed) and 27,000 BVs for Bed B (measured through one bed).
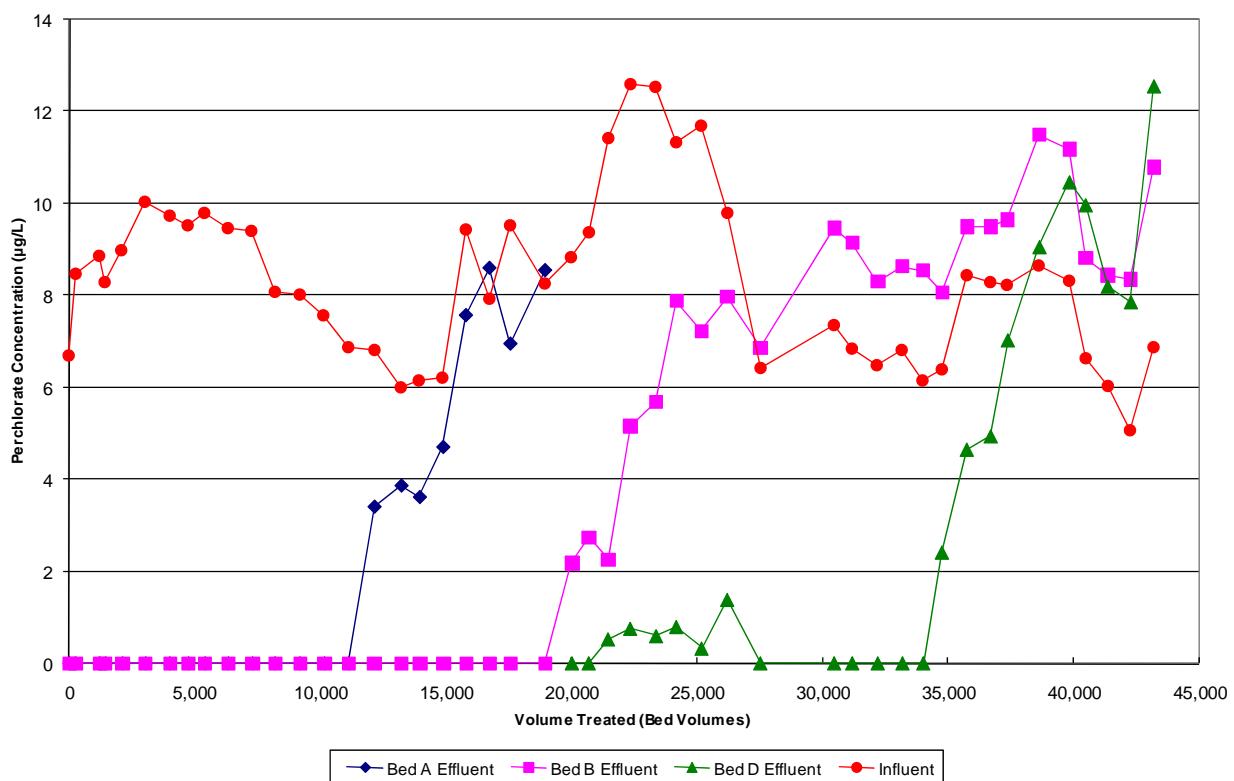
Figure 5. Individual bed breakthrough curves, BVs as measured through one bed.

Bed D was placed in service at 18,000 BVs as the new lag bed while Bed B became the lead bed. A low level of perchlorate breakthrough from Bed D was observed between 21,000 and 26,000 BVs into the demonstration before the concentration reverted to nondetect. Breakthrough clearly occurred at 35,000 BVs and saturation was reached by 40,000 BVs.

Bed C was not tailored and thus was intended only to treat any CPC that leached from the TGAC beds, not to provide significant perchlorate removal. As expected Bed C broke through soon after Bed D (as shown in Figure 5-17 in the full report).

During the later periods of operation, beds B, C and D all reached perchlorate effluent concentrations that exceeded the influent. Thus they showed some evidence of a chromatographic rollover effect.

6.6.2.2 CPC Results

The lead bed, Bed A, showed substantial leaching of CPC immediately after being placed in service, which rapidly declined. The maximum concentration observed from any bed was observed from the lag bed (Bed B) at 4600 µg/L. CPC was never detected in the effluent of the final polishing bed C, suggesting that the provision of a polishing bed was an adequate precaution against the release of the tailoring agent into the treated water.

6.6.2.3 Nitrosamine Results

No nitrosamines were detected in the influent water in any sampling event above the reporting limit of 2 nanograms per liter (ng/L). At system start-up n-nitrosodimethylamine (NDMA) was measured in effluent from the second TGAC bed at 39 ng/L. No other nitrosamines were detected in any other sampling event above the reporting limit of 2 ng/L.

6.6.2.4 General Chemistry Results

With minor exceptions, values of pH, alkalinity, conductivity and TDS were relatively stable in the influent and effluent from the first and second TGAC beds. Alkalinity levels were initially low, and then rose, suggesting that bicarbonate may have initially been sorbed by the TGAC beds before reaching saturation.

6.6.2.5 Anion and Cation Results

Anion and cation concentrations were monitored in the influent and effluent of the 38 GPM TGAC column.

During startup there were relevant differences in concentrations of chloride, nitrate, and sulfate anions, as expected. Initially, chloride effluent concentrations were higher than influent concentrations, which may indicate early sloughing off of the counterion of the CPC surfactant used to tailor the GAC, which may still be associated with it on the bed. At startup (less than 500 BVs treated), nitrate effluent concentrations were less than influent, indicating nitrate sorption by the TGAC. Thus, it is possible that initially nitrate and chloride were exchanging. Sulfate influent and effluent concentrations were approximately equal during startup. After the initial effects there was no statistically significant difference between influent and effluent anion concentrations.

There was no statistically significant difference between the influent and effluent concentrations of potassium, sodium, calcium and magnesium cations.

6.6.2.6 Pressure Data

Pressure data for the lead bed showed a slow, steady increase in pressure drop during the initial operational period, with only slight increases thereafter.

The lag bed pressure drop increased fairly dramatically through the first seven months of operation, then dropped off and held steady. The changes were not correlated with the well operational change or the change-out in the lag bed.

The pressure drop at Bed B, the only bed that served in both lag and lead positions, increased rapidly while in the lag position, then immediately dropped when changed to the lead position. While in the lead position, pressure drop did not appear to increase markedly.

6.6.3 Six Condition Pilot-Scale System Sampling Results

Effluent concentrations were monitored after each of the two stratified beds that comprised each of the six condition systems (Effluent 1 and Effluent 2).

6.6.3.1 Perchlorate Results

Table 2 lists the BVs to breakthrough for perchlorate in each of the six systems. In the Effluent 1 results the perchlorate spike had the most dramatic effect on performance, followed by TDS, TCE, and nitrate. The predisinfectant/oxidant train also underperformed the control. All of the trains except the TCE spiked train displayed substantial evidence of a chromatographic rollover effect.

Table 2. BVs to perchlorate breakthrough in six condition pilot-scale test.
(BVs as measured through one bed)

Train	BVs to Breakthrough		Difference from Control (%)	
	Effluent 1	Effluent 2	Effluent 1	Effluent 2
Control (stratified)	12,794	23,191	Not Applicable	Not Applicable
TCE spiked	9942	21,266	-22	-8.3
TDS spiked	9145	19,940	-29	-14
Nitrate spiked	9966	17,986	-22	-22
Perchlorate spiked	7767	15,894	-39	-31
Predisinfectant/oxidant	10,881	13,863	-15	-40

6.6.3.2 CPC Results

Influent and effluent samples for all conditions were tested for CPC using the titration method; no CPC was detected in any of the samples tested. For samples tested using the LC/MS/MS method, 42.3 ng/mL of CPC was detected from the stratified bed control Effluent 2 port and 16.5 ng/mL from the predisinfectant/oxidant train during the first 2,000 BVs.

6.6.3.3 Nitrosamine Results

In common influent and stratified bed control train effluent samples, no nitrosamines were detected in any sampling event above the reporting limit of 2 ng/L. The only detection was 6.3 ng/L NDMA in an effluent sample of the prechlorination/oxidant train.

6.6.3.4 General Chemistry Results

With a few exceptions, values of pH, alkalinity, conductivity and TDS were relatively stable in influent and effluent samples. As with the 38 GPM system, alkalinity levels in some cases were

initially below influent levels, then rose, suggesting that bicarbonate may have initially been removed by the TGAC beds before reaching saturation. There was variability in the general chemistry of the TDS/sulfate spiked train due to difficulties in controlling the spiking system.

6.6.3.5   Anion Results

With minor exceptions, there was no statistically significant difference between influent and effluent concentrations of bromide, chloride, nitrate, and sulfate anions. The exceptions were caused by a small number of outliers, and no meaning is attributed to them.

The anion behavior just after startup mirrored their behavior during startup of the 38 GPM TGAC system. That is, nitrate effluent concentrations were less than influent (signifying initial sorption of nitrate), chloride effluent concentrations were higher than influent (suggesting exchange of chloride with nitrate), and sulfate influent and effluent concentrations exhibited no trend.

6.6.3.6   TCE Results

In the TCE spiked train, using the second spiking system, TCE breakthrough occurred after perchlorate breakthrough, near the very end of the operation of the TCE train (approximately 11,000 BV). An estimate made by coauthor James Graham of Siemens, using the modeling program IsoCalc predicted breakthrough for TCE at 87,500 BVs for virgin carbon under these circumstances.

6.6.4   SDS Results

The SDS testing showed that the potential for the generation of disinfection by-products following treatment with hypochlorite in the TGAC system is minimal, with the possible exception of the formation of a low concentration (<1 µg/L) of bromoform. There was no greater potential for disinfection by-products following treatment with hypochlorite combined with CPC.

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7.0 PERFORMANCE ASSESSMENT

The performance objectives for the perchlorate systems are listed in Table 1.

7.1 PERCHLORATE CONCENTRATION REDUCTION

The perchlorate concentration reduction objective was to demonstrate that TGAC could reduce perchlorate concentrations below the California DPH notification level (NL), now MCL, of 6 μg/L. TGAC successfully achieved the perchlorate concentration reduction objective for a total treated volume of approximately 30,500 BVs with two beds in series.

7.2 PERCHLORATE MASS REMOVAL AND BREAKTHROUGH VOLUME

The perchlorate mass removal and breakthrough volume objective was to demonstrate that the mass of perchlorate removed per unit volume of TGAC would be sufficient to allow at least six months of treatment with a reasonably sized vessel in a typical application. During the demonstration of the 38 GPM system, the first lead vessel, Bed B and Bed D operated for four to five months as the lead bed before perchlorate saturation. The TGAC approached the mass removal and breakthrough volume objective, but did not achieve it during the demonstration.

7.3 AVOIDANCE OF SECONDARY IMPACTS TO DRINKING WATER

The intent of this objective was to demonstrate that the technology does not cause significant secondary water quality issues. The ability of a TGAC system to comply with MCLs for nitrate is primarily controlled by influent quality since nitrate adsorption occurred only very early in the beds operation and nitrate rollover was not observed. There was no discernable effect of the TGAC technology on metals concentrations, as expected. Limited nitrosamine detections from both field-scale systems did not suggest secondary water quality issues when compared to DPH NLs. CPC leaching was observed initially from the 38 GPM TGAC system beds, but the guard bed prevented CPC from being leached into the treated water, as expected.

7.4 EFFECT OF SECONDARY ANALYTES—TIME TO SATURATION

The effects of different water chemistry parameters on TGAC perchlorate removal were monitored in both bench scale and the six condition field-scale tests. Results of RSSCTs showed that the adsorption of perchlorate is pH dependent, with 50% greater removal at pH 4 than at the natural pH of the groundwater at 8, and 75% greater than at a pH of 10. Nitrate also affected the removal of perchlorate; increasing the nitrate concentration to 60 mg/L and 100 mg/L reduced the removal of perchlorate by 17% and 53%, respectively. Sulfate, thiosulfate, chloride, and bicarbonate did not affect the adsorption of perchlorate up to the MCL. Also, bench-scale experiments showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7.

In the six condition pilot-scale tests, the perchlorate spike had the most dramatic effect on performance, followed by TDS, nitrate, and TCE. The predisinfectant/oxidant train also performed more poorly than the control. All of the trains except the TCE spiked train displayed substantial evidence of a chromatographic rollover effect for perchlorate. Breakthrough and

saturation both occurred 8 to 22% sooner with the TCE spiked system than with the control system.

7.5   EASE OF USE—EASE OF OPERATION AND MAINTENANCE

The objective of the ease of use criterion was to observe O&M labor requirement (time) and level of skill required of the municipal operator, compared to existing IX systems. It was determined that the O&M for a three bed, full-scale TGAC system would be similar to that required for the pilot-scale 38 GPM system, but if more than three beds were utilized in a full-scale TGAC treatment system, additional O&M time would be required to obtain the additional monitoring samples. During the period of operation, these activities are likely to be similar to those required for a similarly sized IX system. However, since IX systems are likely to have a longer time to breakthrough, a greater frequency of monitoring will likely be required for the TGAC system. A faster breakthrough time will also require more operator attention to breakthrough. Faster breakthrough could also lead to more beds being used in TGAC system design, which would increase monitoring costs.

7.6   RELIABILITY/ROBUSTNESS—PERCENTAGE OF TIME IN OPERATION

The objective of the reliability/robustness criterion was to achieve 98% or greater operability. The 38 GPM TGAC system achieved an operational uptime of approximately 97%, including causes of downtime that had little or nothing to do with the TGAC technology itself.

7.7   COST REDUCTION—REDUCED TREATMENT COSTS

The objective of this performance metric was to reduce treatment costs significantly over IX technology by reducing waste disposal and/or use of lower priced TGAC compared to resin. Section 8 includes a discussion of economic issues.

7.8   SCALING

The experimental design of the project was intended to allow scalability to be qualitatively evaluated. Three scales were compared: (1) RSSCT, (2) 1.5 to 3 GPM (six condition pilot-scale test), and (3) 38 GPM (main demonstration).

Crittenden et al. (1986, 1991) pioneered the use of RSSCTs as a rapid method for the design of large-scale fixed-bed GAC adsorbers, and developed and tested scaling equations for designing full-scale adsorbers based upon the results obtained from small column RSSCTs. To apply RSSCT results to simulate a large-scale adsorber, particle size (of the medium), hydraulic loading, and EBCT must be properly up-scaled. When internal diffusion controls the adsorption rate so that the intraparticle diffusivity is a linear function of particle size (referred to as proportional diffusivity), a critical exponent in the scaling equation is equal to 1. For some other applications where the exponent is equal to 2, a relationship known as constant diffusivity is simulated.

7.8.1 Comparison between RSSCT and Demonstration Scales

The results from the 38 GPM system showed a lesser capacity for TGAC to adsorb perchlorate than what was observed with the RSSCT that employed proportional diffusivity similitude. There are several possibilities for such a distinction: (a) there could be redox-sensitive species in this water that in an intermediate-valent state pose considerable competition with perchlorate, but when further oxidized pose less competition; (b) proportional diffusivity is not the appropriate similitude to use when sorbing perchlorate onto surfactant tailored media; (c) the pore volume distribution of the GAC used in the pilot-scale tests was different from that used in the RSSCTs to pose a considerable difference; (d) microorganisms decomposed the surfactant and rendered it unable to sorb perchlorate; (e) downtime that was experienced at field-scale that was not experienced at bench-scale affected performance; and (f) perhaps a portion of the field-scale beds bypassed/short-circuited.

Recent tests conducted at PSU suggest that a similitude intermediate between proportional and constant diffusivity, one where the exponent equals 1.5, may be the most appropriate way to use RSSCTs to predict field-scale perchlorate performance for TGAC. Thus, of the various possibilities explored, this difference in similitude would appear to best explain the observed lack of RSSCT to field-scale correlation.

7.8.2 Comparison between Two Field Scales Tested

Semi-quantitatively, the 1.5 and 3 GPM tests in the six condition pilot-scale test reasonably agreed with the 38 GPM system performances at Fontana. This is an expected result since these two scales were run at essentially the same EBCT; thus the similitude approach of Crittenden et al. (1986, 1987, 1991) is not required for this comparison. A comparison of the stratified bed control to the 38 GPM results suggests that the use of stratified beds did not produce significantly different results when compared to the design in which the tailored and untailored carbon were in separate beds.

7.8.3 Scalability Summary

Unexpectedly, the RSSCT did not accurately predict the full-scale performance in the Fontana demonstration. The comparison between the two field-scales tested suggests that full-scale performance can be predicted from small pilot tests; however, the small-scale pilot tests would have the disadvantage of requiring a time equivalent to the full-scale EBCT for performance. Thus it is desirable to improve the ability of the RSSCTs to predict full-scale performance for this technology, which can be done as follows:

- In waters known to be at least mildly reducing (negative redox potentials) and thus to potentially contain unstable reduced sulfur species (See Appendix C of full final report), perform the RSSCTs at the field site or with very fresh samples.

- Use an exponent of 1.5 in the Crittenden et al. (1986, 1987, 1991) similitude equation to relate RSSCT data to full-scale data for TGAC applications.

- Carefully select the GAC tested by RSSCT to match the field carbon both as regards the general GAC type (bituminous versus anthracite for example) as well as pore size distribution.

8.0   COST ASSESSMENT

Any innovative technology, in order to successfully transition to commercial use, must be cost competitive with established technologies. This section describes a model that was developed by AFIT to predict the cost of using the TGAC technology to treat water of a specified quality. The model accounts for the presence of anions that compete with perchlorate for sorption sites on the TGAC. The model is then applied to help identify key factors that drive TGAC technology cost.

8.1   COST AND PERFORMANCE MODEL

A TGAC cost model was developed during this project to predict TGAC performance and life-cycle costs to treat perchlorate-contaminated water for various influent water quality and technology operating conditions (Powell, 2007; Craig, 2008). Using inverse modeling, the model's design parameters were obtained from the laboratory RSSCTs. Cost data used in the model were based on conventional GAC installations, modified to account for tailoring.

The cost and performance submodels described here should not be viewed as fully quantitative design tools, but rather as screening models that can be applied to help a user qualitatively understand how the cost and performance of the TGAC system will vary in response to changes in environmental and operational conditions. Our analysis suggests that the full-scale performance prediction inaccuracies caused by scaling issues and the use of anthracite-based rather than bituminous-based TGAC roughly cancel each other; therefore the economic analysis presented here should be reasonably reliable for use in technology screening.

8.1.1   Performance Submodel

Parameter values were established based on a best fit of the model to experimental results obtained from 12 RSSCTs (Craig, 2008). The model, originally developed by Powell (2007), minimizes "total error" to obtain the best fit. The total error is defined as the sum of the percent differences between the model-predicted and observed BVs to breakthrough for the different RSSCT runs. Given a design flow rate, an EBCT for a TGAC column, column configuration (series or stand-alone) and concentrations of perchlorate and competing anions in the influent water, the model predicts BVs of water that can be treated before TGAC replacement is needed.

8.1.2   Cost Submodel

The cost model developed by Craig (2008) for TGAC technology used cost data from the USEPA for GAC installations that treated 2500 gallons per day to 1 million gallons per day (MGD) (USEPA, 1979). These data were used to develop construction and O&M cost curves based on empirical expressions for cost as a function of treatment capacity (GPM). Additional cost elements specific to TGAC were included in the model: the cost of tailoring the GAC; additional media, disposal and transport costs; and the cost of replacing the spent TGAC and conventional GAC. Additional information on development of the cost model is available in Powell (2007) and Craig (2008).

In our analysis, the capital cost in 2007 dollars was converted into equivalent annual costs using the capital recovery factor over a 20-year planning horizon. This annualized cost was then added to the annual O&M costs (assumed to be constant) to derive a total annual cost. Additionally, the

model used a 2.8% real interest rate as specified by the Office of Management and Budget (OMB) Circular A-94 (OMB 2009). The real interest rate represents the time value of money adjusted for inflation.

8.1.3 Combined Cost and Performance Model

The performance submodel determined the BVs of water that can be treated, which was then used as input for the cost submodel. The final output of the cost and performance model was the cost of treatment per acre-ft of water. The output included both the total O&M cost and the capital cost (both total and annualized based on the amortization period and the given discount rate).

8.1.4 Application of Model to Predict 38 GPM Field Demonstration Costs

The cost and performance model was used to predict the capital and O&M costs of the 38 GPM field demonstration system at Fontana (Tables 3 and 4). The difference between the model prediction and the actual capital costs was 0.6%. The difference between the model-estimated annual costs and the actual annual O&M costs was 27.6%.

Table 3. Capital costs for Fontana 38 GPM field demonstration.
(Craig, 2008)

Capital Cost Elements	Model Estimated Costs	Actual Costs	Explanation of Field Expenses
Site preparation	$2500	$5530	Based on 50-50 split of 38 GPM and 6-Condition Column costs[1]
Manufactured equipment	$30,140	$76,840	Includes all expenses needed to produce, transport, install, and start-up the system on site[2]
Tailoring GAC media cost (CPC)	$15,600[4]		
Pumps, piping, and valves	$11,810		
Miscellaneous and contingency	$12,240	$12,240	Engineering and design drawings
Electrical and instrumentation	$1630	$3630	Based on 50-50 split of 38 GPM and 6-Condition Column costs[3]
Labor	$23,730		Labor costs were included in expenses and not broken out separately
Total Capital Costs	**$97,650**	**$98,240**	Deviation of 0.6%

[1]Total site preparation expense was $11,050 for the entire Fontana demonstration. Site preparation cost for the 38 GPM plant is considered to be half.
[2]Complete cost to furnish the TGAC system was $86,200. This cost includes media change-out and installation of Bed D. To discount this media-change-out, $9356 was subtracted; bed volume: 375 gallons (approximately 1562 pounds of TGAC media in each vessel); $5.99/lb CPC-tailored TGAC media (Peschman, 2007); 1,565 lb×$5.99/lb = $9356).
[3]Total electrical and instrumentation expense was $7250 for the entire Fontana demonstration. Electrical and instrumentation cost for 38 GPM plant was considered to be half.
[4]Tailoring media cost is based on demonstration media expenses ($5.99/lb) minus estimated conventional GAC cost ($1.00/lb) (Cannon, 2007); 1565 lb/bed×$4.99/lb×2 beds = $15,619.

Table 4. O&M costs for Fontana 38 GPM field demonstration.

O&M Cost Elements	Model Estimated Annual Costs	Actual Annual Costs	Explanation of Field Expenses
Energy costs	$500	$500	Model electricity costs estimated at $0.0616 per kW-hr and actual Fontana electricity costs estimated at $0.0633 per kW-hr
Maintenance material costs	$1200	$9800	Maintenance material costs assumed to be 10% of the capital cost
Labor costs	$8500	$8300	Model predicted 161 hours per year and actual hours per year was 156. Hourly wage rate of $53 per hour used
Total media costs	$35,000	$36,025	Model predicted carbon utilization rates (CURs) utilized. Actual cost assumes GAC (@ $1.68 per lb) in guard bed is replaced annually (1500 lb per year) and TGAC (@$5.99 per lb) is consumed at the model predicted CUR (5600 lb per year).
Disposal	$600	$15,000	Actual cost based on contract cost
Transport	$4600		
Total O&M Cost	$50,400	$69,625	Deviation of 27.6%

8.2 COST DRIVERS

The major cost driver for the TGAC technology, accounting for 70% of total cost, is the cost of the media. As the cost of TGAC decreases with expanded production, the overall cost of the TGAC technology would be expected to decrease accordingly.

Sensitivity analyses were conducted using the cost and performance model to estimate how individual parameter values affected overall cost. The effects of the following parameter values and operational characteristics on cost were evaluated: flow rate, influent water quality, parallel versus series operation, media regeneration versus replacement, vessel size, TGAC mesh size, and EBCT. With regard to flow rate, the model predicted significant economies of scale, and as the flow rate increased, treatment costs per unit ($ per acre-foot) decreased. However, above 400 GPM, the decreases in unit costs with increases in flow rate were greatly diminished. Other findings of the sensitivity analyses were that influent nitrate concentration had a strong effect on relative unit costs, and that cost increases with decreasing EBCT, in agreement with findings for typical GAC operations by Faust and Aly (1998).

8.3 COST ANALYSIS

8.3.1 Cost of Competing Technology

As a result of recent technological and process improvements, the general cost of IX water treatment for perchlorate has declined steadily since its early use. Siemens (2007) estimates IX treatment costs for perchlorate removal in 2007 to be in the range of $75 to $100 per acre-ft; a significant decline from cost estimates in 2000, when treatment costs ranged from $450 to $650 per acre-ft. The decline in treatment cost is attributed to improved resin selectivity and perchlorate capacity, regulatory acceptance of selective resin technology, and reduced resin costs. Thus, during the technology development timeline for the TGAC technology, the cost of

competing technologies has dropped approximately five-fold. This has made the task of developing a less costly solution for perchlorate treatment than IX much more difficult.

8.3.2 Cost Analysis for TGAC at Fontana California Full-Scale

Based on various operating assumptions (8.4 minute EBCT, 2000 GPM water flow rate, series operation, media regeneration [regeneration was not demonstrated in this project]) the cost and performance model was applied to estimate costs to treat Fontana water at large-scale using TGAC (Table 5). The major cost driver for the TGAC technology, accounting for 70% of total costs, is the cost of the media. Capital and labor costs are the next highest drivers at 11% and 9%, respectively. At the current very small-scale production, TGAC media costs are relatively high ($5.99 per lb). As the cost of TGAC decreases with expanded production, the overall cost of the TGAC technology would be expected decrease accordingly.

Table 5. Relative and absolute costs for TGAC treatment of Fontana water by cost element.

Cost Element	Cost ($ per acre-foot, rounded to nearest $1)	Proportion of Cost (rounded to nearest 1%)
Annualized capital costs[1]	$34	11%
Energy costs	$8	3%
Maintenance material costs	$20	6%
Labor costs	$27	9%
Total media costs	$211	70%
Disposal[2]	$0	0%
Transport	$2	1%
Total	$302	100%

[1]Capital cost elements as indicated in Table 3.
[2]Disposal costs are negligible, since regeneration of TGAC is assumed.

8.3.3 Cost Analysis for TGAC at a Typical Site

To illustrate use of the cost and performance model, costs were calculated for a hypothetical, typical treatment scenario. The estimated capital and operating costs for treatment with TGAC were $261 per acre-ft. The estimated costs for the same system using IX were $135 per acre-ft. In order for TGAC technology to be cost competitive with IX, technology costs would have to decrease significantly, for instance, through expanded TGAC production. Another caveat is that the TGAC media, the largest cost driver, had costs based on the pilot-scale study. Presumably, full-scale production costs will be considerably less.

The presence of nitrate inhibits perchlorate adsorption on TGAC. Thus a higher nitrate concentration should result in an increased treatment cost. Doubling the nitrate concentration in the water from 10 mg/L to 20 mg/L increased the treatment cost per acre-ft by 34%.

The field scale testing used TGAC prepared from anthracite-based carbon. Although bituminous-based carbon would have been more effective, that change alone would not have been enough to economically displace perchlorate selective resins.

Further analysis was conducted to determine if TGAC is an economically viable technology to treat plumes of perchlorate comingled with other organic contaminants (e.g., nitroaromatic

compounds or chlorinated solvents) using a model developed by Downen (2009). The range of costs predicted for TGAC treatment of perchlorate-contaminated water with an organic co-contaminant, approximately $200 to $1000 per acre-ft, is comparable to the costs of using conventional technologies to treat water with cocontaminants.

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9.0 IMPLEMENTATION ISSUES

9.1 REGULATORY REQUIREMENTS

The water produced and treated during the pilot testing was disposed of in the FWC percolation pond at the site using an existing NPDES discharge permit (because the water from the demonstration was not used as drinking water). Application of the TGAC technology to treat drinking water would not require a NPDES permit; however, a discharge permit may be required for the disposal of backwash water and other process water (e.g., water used during disinfection of the vessels and piping, etc.) that is generated during normal operation of the treatment system. A TGAC drinking water treatment system would need to be permitted through the appropriate permitting agency as required in the state of operation prior to being used as a drinking water treatment technology. For example, in California, all drinking water treatment systems must be permitted through the DPH. DPH in turn would require NSF certification of the TGAC manufacturing facility.

Disposal of the spent TGAC was conducted in accordance with DOT and RCRA regulations. These regulations would also need to be adhered to in a full-scale application of the treatment technology.

Siemens produced the TGAC for this project at their Los Angeles, CA, facility. This facility was equipped to process waste waters such as those that contain CPC—the tailoring agent used during this demonstration. The only CPC discharge from the tailoring process occurred during the final rinsing process. During the rinsing operation, CPC that was present in the rinse water was removed by pumping the rinse water through a bed of virgin GAC prior to being discharged. This partially tailored bed could be used in the manufacture of subsequent batches of TGAC. The spent 10-micron particulate filters generated during the demonstration were air-dried on site, and then disposed of as municipal waste since no VOCs were present in the influent water. A TGAC treatment system that is used to treat both perchlorate and a VOC may require disposing of spent particulate filters as a solid waste that may require characterization. No other residuals requiring disposal were generated by the tailoring process.

9.2 OTHER REGULATORY ISSUES

Building permits for the construction of the demonstration system were not required by the City of Fontana. Depending on the jurisdiction, building and safety permits may be required for construction of a full-scale TGAC treatment system.

Because this project was a demonstration of a drinking water treatment technology, the DPH was presented with information regarding the project and the results of the project. Copies of this report, and other project information, will be forwarded to the appropriate personnel at DPH with ESTCP approval and guidance. Other interested regulatory agencies such as the California Regional Water Quality Control Board (RWQCB), California Department of Toxic Substances Control (DTSC), and the NSF will also be provided with applicable documents as approved or requested by ESTCP, or other involved agency. Public participation was not included in the demonstration.

9.3   END-USER ISSUES

The California DPH is believed to be the state regulatory agency in the United States with the most experience with perchlorate issues in drinking water. Stakeholders for this technology included water utilities, water purveyors, and potentially responsible parties for any given perchlorate plume. Endusers are the general public (drinking water customers), agricultural (crop irrigation and livestock) operations, and commercial, industrial and government facilities. From a stakeholder/end-user perspective, the economic costs/issues are important; based on current full-scale estimates, the TGAC will cost more than current methods, for example, single-use IX with incineration of spent resin as the predominant disposal technique.

The results of this project showed that:

- Bituminous-based carbons are superior to anthracite-based carbons in preparing TGAC for perchlorate treatment.

- Neither isotherm testing, RSSCTs, nor any other known bench-scale protocol, is able to perfectly predict field-scale performance in a rapid laboratory treatability test.

- A similitude intermediate between constant and proportional diffusivity, one with the exponent equal to 1.5 may be the most appropriate way to use RSSCTs to predict field-scale perchlorate performance for TGAC.

TGAC also has several perceived or potential limitations not found with other treatment technologies. These limitations include the following:

- TGAC has a lower perchlorate capacity than most IX resins and will require more frequent change-outs because a smaller volume of water can be treated prior to perchlorate breakthrough/saturation. This limitation may become more pronounced as new, higher perchlorate capacity IX resins are developed.

- TGAC requires a lower hydraulic loading rate (GPM per sq ft), or a longer contact time (EBCT) than IX, and thus more or larger vessels (additional capital cost) will be required to treat a given flow rate of water. Additionally, if TGAC were to be implemented at an existing IX facility, additional vessels would need to be installed.

- If applied to a mixed-contaminant water (e.g., perchlorate and VOCs) perchlorate and the VOCs may reach breakthrough at different times, which would require an early change-out, and thus a reduced capture efficiency for VOCs or perchlorate than two separate media (such as those found at existing perchlorate and VOC treatment facilities that utilize both conventional GAC and IX resin).

- TGAC may leach small concentrations of the tailoring agent into treated water. Some state agencies may require the addition of a "guard" bed to capture residual tailoring agent.

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